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SPECIAL FEATURES OF THE THEORY OF THERMAL EXPLOSION IN A REACTION WITH UNBRANCHED CHAINS

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In studying the theory of thermal explosion, the author used the dependence of the rate of heat liberation on the temperature of the gas (derived from kinetic measurements conducted at a low temperature and at a slow reaction rate under isothermic conditions).

The nature of the mechanism for establishment of equilibrium of the dissociation $Br_2 \rightleftarrows 2Br$ (on the surface of the vessel or in the volume of the gas) cannot affect the reaction because, thermodynamically, the equilibrium concentration of atoms at a given temperature is always the same and does not depend on the reaction mechanism.

When the reaction occurs under ignition conditions, the temperature of the gas differs from the temperature of the wall of the container; therefore, the concentration of atomic bromine is dependent on the reaction mechanisms of the dissociation and recombination of bromine.

The kinetic expression which Kokochashvili used previously [1], based on a tacit assumption that all reactions (including dissociation) proceed in the volume, has the form:

$$W = const \cdot e^{\frac{-40,000}{RT}} = const \cdot e^{\frac{-46,000}{2RTg-}} \cdot e^{\frac{-17,000}{RTg-}} [H_2]\sqrt{[Br_2]}, \quad (1)$$

where 46,000 calories is the energy of dissociation of bromine, and 17,000 calories is the heat of activation of the reaction $Br + H_2 = HBr + H$.

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If the dissociation proceeds on the wall of the vessel (while the actual chain reaction $Br + H_2$, $H + Br_2$ proceeds in the volume of the gas), the expression can be reduced to:

$$W = const \cdot e^{\frac{-46,000}{2RT_w}} \cdot e^{\frac{-17,000}{RTg}} \; [x_2] \; \sqrt{[Br_2]} \, , \qquad (2)$$

where T_w and T_g represent the temperatures of the container wall and the gas.

If calculations of the critical conditions for a thermal explosion are carried out on the basis of (2), the equation for the critical heating will be $\Delta T = RT^2/17,000$ instead of $\Delta T = RT^2/40,000$.

At a given temperature, if the dissociation equilibrium is established at the container wall, then the critical ignition pressure must be higher than the value $(40,000/17,000)^{1/2}$, i.e., 1.8 times higher than the ignition pressure of the same reaction in the case of volume dissociation.

The occurrence of one or the other process is determined by the following two factors: the catalytic activity of the surface and the degree of the geometric extent of the chain, i.e., the average distance over which the atoms of bromine are diffused from their point of origin. This distance was found by considering the distance over which the disturbance of the concentration of atomic bromine spreads rather than the path of a given individual bromine atom.

L. C. Kassel' [2] has developed an equation for the recombination rate of bromine atoms (the concentration in molecules per cubic centimeter, and the time in seconds):

$$\frac{d[Br_2]}{dt} = 3 \cdot 10^{15} [Br]^2 [x]. \qquad (3)$$

Kokochashvili set out to calculate the constant for the recombination rate independent of the temperature. If the dissociation is calculated, the equation for the variation in the concentration of bromine atoms has the form:

$$\frac{d[Br]}{dt} = -6 \cdot 10^{15} [Br]^2 [x] + K_{dis}[Br_2][x] \qquad (4)$$

where K_{dis} is the constant of the rate of dissociation of bromine in the reaction $Br_2 + [x] = Br + Br + [x]$.

To eliminate the necessity of determining K_{dis} separately, the obvious thermodynamic connection between the direct and reverse reactions is employed. With the equilibrium concentration of bromine atoms designated as $\{Br\}$, the rate of both reactions is obviously equal to:

$$K_{dis}[Br_2][x] = 6 \cdot 10^{15} \{Br\}^2 [x]. \qquad (5)$$

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Substituting (5) and (4), the following expression is obtained:

$$\frac{d[Br]}{dt} = 6 \cdot 10^{15}[x]([Br]^2 - [Br]^2). \tag{6}$$

At a concentration close to equilibrium $[Br]-\{Br\} \ll \{Br\}$, resolution into a series gives:

$$\frac{d}{dt}([Br]-\{Br\}) = -12 \cdot 10^{15}[x]\{Br\}([Br]-\{Br\}). \tag{7}$$

This equation is used to determine the characteristic time for the establishment of equilibrium of the dissociation of bromine:

$$\tau_{dis} = \frac{1}{12 \cdot 10^{15} \cdot [x] \cdot \{Br\}}, \tag{8}$$

$$\frac{d}{dt}([Br]-\{Br\}) = -\frac{1}{\tau_{dis}}([Br]-\{Br\}). \tag{9}$$

The case in which the concentration of the diffused atoms of bromine in one place e.g., on the container wall, differs from the equilibrium concentration in the gas was investigated by Kokochashvili, using the following equation for the diffusion of atoms of bromine (taking into account their dissociation and recombination):

$$\frac{d}{dt}([Br]-\{Br\}) = D\Delta([Br]) - \{Br\})\frac{1}{\tau_{dis}}([Br] - \{Br\}). \tag{10}$$

For duffusion in unlimited space and under conditions constant in time this equation has the form:

$$([Br]-\{Br\}) = Ae^{\frac{-x}{\sqrt{D\tau}}} \tag{11}$$

Any local disturbance of the concentration of Br extends only over a space interval of the order of $L = \sqrt{D\tau}$.

Kokochashvili noted the variance of his equation (10) with respect to Bursian's and Sorokin's equation for branched chains. In the case of branched chains, the member dependent on the reaction has another value; the solutions are not exponents, but sines and cosines. Therefore, the equation for branched chains gives the critical conditions of explosion, whereas equation (10) does not disclose critical conditions.

For practical purposes, Kokochashvili assumed that $D = \chi = \lambda/c$, P. At a given composition of the gaseous mixture, the diffusion coefficient is inversely proportional to the total concentration of the mixture $[x]$. For a stoichiometric mixture of hydrogen with bromine

$$D = \frac{1 \cdot 7 \cdot 10^{-5}}{x} \quad \text{and} \quad L = \frac{4 \cdot 10^{-11}}{[x] \sqrt{\{Br\}}}.$$

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Making use of the constant for the dissociation equilibrium of bromine as given by Lewis and Elbe /3/, Kokochashvili carried out the computation of all values for the mixture $H_2 + Br_2$ on the boundary of ignition at T equals 800 degrees K and P equals 50 millimeters of Hg. Under such conditions, /x/ $10^{-6} \frac{mol}{cm^3}$.

$$[H_2] = [Br_2] = 5 \cdot 10^{-7} \frac{mol}{cm^3} ,$$

$$\{Br\} = 1 \cdot 2 \cdot 10^{-9}; \quad T = 0.07 \text{ sec},$$

$$D = 17 \frac{cm^2}{sec}; \quad L = 1.1 \text{ cm}.$$

From these relationships it can be seen that, under the above conditions, the distance L of diffusion of the atoms is fully in conformity with the dimensions of the vessel. The maximum distance from the central point to the wall is 1.5 centimeters, but the average is even less. (The author found it very difficult to make a quantitative examination in this instance.) If the diameter of the reaction vessel was many times more than L (10 or 20 centimeters), the concentration of bromine atoms at any given point would depend on the temperature of the gas; the container wall would affect a small portion of the mixture, and kinetic equations derived from homogeneous kinetics could be used unconditionally. In such large vessels it can be assumed that treatment of the surface with KCl would not affect the reaction rate and the self-ignition limits.

In vessels with medium and small diameters, the average concentration of bromine atoms under conditions of thermal explosion, i.e., at differing temperatures of the gas and the container wall, should depend on the composition of the surface.

In the limiting case where the vessel's diameter is less than L, the ignition pressure on a surface which is perfectly inactive catalytically should be 1.8 times less than the ignition pressure in a vessel whose surface develops an equilibrium concentration of bromine atoms in its vicinity. Experimentally, the ignition pressure in a vessel treated with KCl (i.e., with an only slightly active surface) is less than the ignition pressure in an untreated vessel by a factor of 1.37 at 420 degrees Centigrade, 1.5 at 500 degrees Centigrade, 1.3 at 560 degrees Centigrade, and 1.2 at 600 degrees Centigrade. These values are in accordance with the developed conception (all values lie between one and 1.8), in consideration of the fact that medium-sized vessels were used.

Finally, Kokochashvili examined the time aspects of the reaction with unbranched chains.

The generally used expression $const \dfrac{[H_2] \sqrt{[Br_2]}}{1 + \dfrac{[H\,Br]}{10[Br_2]}}$ was derived by the method of stationary concentrations, i.e., under the assumption that the bromine atoms are in equilibrium. Previously in this article, the time in which the dissociation equilibrium of bromine molecules is established was determined. Kokochashvili compared this time with the total time consumed in the reaction $H_2 + Br_2$ determined to establish the limits for the usability of the method of stationary concentrations, a matter treated in a general way by N. N. Semenov /4/ and D. A. Frank-Kamenetskiy /5/.

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Kokochashvili arrived at an equation for the variation in the concentration of molecular hydrogen or molecular bromine

$$\frac{d[Br_2]}{dt} = \frac{d[H_2]}{dt} = -K[Br][H_2], \qquad (12)$$

where K is the constant for the rate of the reaction $Br + H_2 = Hbr + H$ and, in conformity with Jost [7], $K = 2 \cdot 10^{12}\sqrt{T} \cdot e^{-\frac{17,600}{RT}}$.

On the basis of this equation, the performance time of the reaction is equal to:

$$\tau_{react} = \frac{1}{K[Br]} .$$

At T equals 800 degrees K, and τ_{dis} equals 0.07 second, τ_{react} equals the order of 0.8 second; i.e., the time of the reaction is considerably greater than the time for the establishment of equilibrium, and for that reason it is correct to use the stationary concentrations method.

By comparison of the expressions $\tau_{dis} = \frac{1}{12 \cdot 10^5 [Br]/x/}$ and $\tau_{react} = \frac{1}{K[Br]}$, it can be seen that at a given $\bar{x}$ or at a constant maximum pressure τ_{react} depends on the temperature more than τ_{dis}, because of the exponential dependence of K on the temperature. That is why, at low temperatures, in Bodenstein's and Lind's experiments [8] τ_{dis} is negligibly small in comparison with τ_{react}.

During a temperature increase, a constantly increasing range of acceleration of the reaction rate should appear at the beginning of the kinetic curve; this phenomenon, like the period of induction, depends on accumulation of bromine atoms.

The period of induction should be greater at increased temperatures within the ignition limits, because then a decrease in /x/ occurs along with the increase in K.

One of the possible causes for the difficulty in obtaining ignition at high temperatures is the fact that part of the mixture burns up during the induction period. This fact was noted by Kokochashvili in comparing theoretical and experimental data /6, 1/.

In conclusion, gratitude for assistance is expressed to Academician N. N. Semenov and Corresponding Member Ya. B. Zel'dovich.

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